



UNIVERSITY  
OF TASMANIA

# Spectroscopic Detection and Hyphenated Techniques in Microfluidic Enabled Gas Chromatography

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A thesis submitted in fulfilment of the requirements for the  
Degree of Doctor of Philosophy



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31-08-2018 A.D.

## DECLARATION

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## LIST OF PUBLICATIONS

1. R. Gras, J. Luong, R.A. Shellie, Direct measurement of trace elemental mercury in hydrocarbon matrices by gas chromatography coupled with ultraviolet photometric detection, *Anal. Chem.* 87 (2015) 11429-11432.
2. R. Gras, J. Luong, R.A. Shellie, Gas chromatography with diode array detection in series with flame ionisation detection, *J. Chromatogr. A* 1500 (2017) 153-159.
3. R. Gras, J. Luong, R.A. Shellie, Gas chromatography and diode array detection for the direct measurement of carbon disulfide in challenging matrices, *Anal. Methods* 9 (2017) 3908-3913.
4. R. Gras, J. Luong, R.A. Shellie, Direct measurement of elemental mercury using multi-dimensional gas chromatography with microwave induced helium plasma atomic emission spectroscopy, submitted to *ACS Earth and Space Chem.* 2 (2018) 471-478.
5. R. Gras, J. Luong, M. Pursch, R.A. Shellie, Positive temperature coefficient compensating heating for analytical devices, *Anal. Chem.* 90 (2018) 6426-6430.
6. R. Gras, J. Luong, R.A. Shellie, Miniaturized Micromachined Gas Chromatography with Universal and Selective Detectors for Targeted Volatile Compounds Analysis, *J. Chromatogr. A* article in press, September 2018, doi.org/10.1016/j.chroma.2018.08.064.
7. R. Gras, J. Luong, P.R. Haddad, R.A. Shellie, Gas chromatography with simultaneous detection: Ultra-violet spectroscopy, flame ionization, and mass spectrometry, *J. Chromatogr. A* 1563 (2018) 171-179.
- 8\*. M. Lin, R. Gras, C. Bleile, K. Gras, J. Luong, R. A. Shellie, Gas chromatography with reduction gas detection for the characterization of parts-per-billion level of ethylene in various matrices, *LC-GC* 33 (2015) 332-338.
- 9\*. K. Gras, J. Luong, M. Lin, R. Gras, R. A. Shellie, Determination of ethylene glycol in lubricants by derivatization static headspace gas chromatography, *Anal. Methods* 7 (2015) 5545-5550.
- 10\*. J. Luong, R. Gras, K. Gras, R.A. Shellie, Piston cylinder based micro liquid-liquid extraction with GC-qMS for trace analysis of targeted chlorinated organic compounds in water, *Can. J. Chem.* 93 (2015), 1283-1289.
- 11\*. M. R. Jacobs, R. Gras, P.N. Nesterenko, J. Luong, R.A. Shellie, Back-flushing and heart cut capillary gas chromatography using planar microfluidic Deans' switching for the separation of benzene and alkylbenzenes in industrial samples, *J. Chromatogr A* 1421 (2015) 123-128.

- 12\*. J. Luong, X. Guan, S. Xu, R. Gras, R. A. Shellie, Thermal independent modulator for comprehensive two-dimensional gas chromatography, *Anal. Chem.* 88 (2016) 8428–8432.
- 13\*. K. Gras, J. Luong, R. Gras, R. A. Shellie, Trace-level screening of dichlorophenols in processed dairy milk by headspace gas chromatography, *J. Sep. Sci.* 39 (2016) 3957–3963.
- 14\*. J. Luong, R. Gras, M. Hawryluk, R. Shearer, A brief history and recent advances in ozone-induced chemiluminescence detection for the determination of sulfur compounds by gas chromatography, *Anal. Methods* 8 (2016) 7014–7024.
- 15\*. M. Lin, K. Lin, A. Lin, R. Gras, J. Luong, Ultra-trace analysis of furanic compounds in transformer/rectifier oils with water extraction and high-performance liquid chromatography, *J. Sep. Sci.* 39 (2016) 2777–2784.
- 16\*. T. Hayward, R. Gras, J. Luong, Flow-modulated targeted signal enhancement for volatile organic compounds, *J. Sep. Sci.* 39 (2016) 2284–2291.
- 17\*. J. Luong, R. Gras, R.A. Shellie, Differential ion mobility spectrometry with temperature programmable micromachined gas chromatography for the determination of bis(chloromethyl)ether, *Anal. Methods* 9 (2017) 5003–5008.
- 18\*. R. Gras, Y. Hua, J. Luong, High throughput gas chromatography for volatile compounds analysis by fast temperature programming and adsorption chromatography, *J. Sep. Sci.* 40 (2017) 1979–1984.
- 19\*. J. Luong, R. Gras, R.A. Shellie, A simplified approach in flow controlled multidimensional gas chromatography, *Anal. Methods* 9 (2017) 2835–2839.
- 20\*. Y. Hua, M. Hawryluk, R. Gras, R. Shearer, J. Luong, Flow injection gas chromatography with sulfur chemiluminescence detection for the analysis of total sulfur in complex hydrocarbon matrices, *J. Sep. Sci.* 41 (2018) 469–474.
- 21\*. J. Luong, Y. Hua, R. Gras, M. Hawryluk, *In situ* methanation with flame ionization detection for the determination of carbon dioxide in various matrices, *Anal. Methods* 10 (2018) 1275–1279.

*\*Research papers published outside of UTAS curriculum activities.*

## ABSTRACT

This thesis introduces newly innovated techniques and associated novel method developments in gas chromatography.

There are two major emphases presented in this work: The first emphasis is in improving selectivity, sensitivity, and portability of analytical instrumentation with the use of molecular spectroscopy technique as a gas phase detector. Performance, benefit, and impact of using spectroscopic techniques with focus on ultraviolet (UV) detection were investigated first with a gas phase photometer and subsequently with a diode array detector. As a selectable multi-wavelength UV based detector, the diode array detector was originally designed for liquid chromatography but successfully repurposed for gas chromatography. Contemporary diode array detector brings ultraviolet – visible spectroscopy onto the capillary gas chromatography timescale. The range of analytes compatible with this detector was substantially expanded to include active compounds enabled by effective passivation techniques and to semi-volatile compounds with boiling point equivalent to hexadecene (285 °C) with the augmentation of a purposely designed heated optical cell. The optical cell was powered by a highly compact isothermal semiconductor positive temperature coefficient heater offering substantial benefits for miniaturized and portable analytical devices in key aspects such as safety in overheating, energy efficiency, size, scalability, and in discovering new thermal management strategies. The user-selectable multi-wavelength, over a range of 190–640 nm affords efficient and effective analysis of many volatile and semi-volatile organic compounds.

The second emphasis focuses on benefits of combining selective detection with contemporary planar microfluidic devices. Hyphenation, multi-hyphenation, and multidimensional approaches enhance analytical capabilities without compromising performance nor incurring additional



analytical time. These approaches have resulted in the development and implementation of innovative analytical methods to address challenging problems encountered in the community of practice. When correctly applied, selective detection can substantially ease the burden of separation traditionally imposed on the analytical column, especially in complex sample matrices. Selective and sensitive detection are enablers to high-speed gas chromatography which are also critical components in the development of portable and hand-held analytical devices. Therefore, research conducted in this field is essential to the capability of sustainable development for gas chromatographic techniques. The synergy in combining a selectable multi-wavelength UV based detector with other contemporary selective detectors and hyphenated techniques like atomic emission detector (AED), micromachined differential mobility spectrometer ( $\mu$ DMS), and the mass spectrometer (MS) operating in selected ion monitoring mode was illustrated in challenging industrial applications.

In this work, critical development, use, and implementation of planar microfluidics in capillary gas chromatography were realized with multiple chromatographic system configurations. The successful use of these devices for mid-point and post column backflush, for hyphenated techniques, and multi-dimensional gas chromatography are highlighted.

## **CHAPTER 1 INTRODUCTION**

### **1.1 Background**

Invented more than one century ago, chromatography is currently one of the most utilized techniques by the analytical community. Specifically, gas chromatography (GC) has been found to be an ideal and practical analytical approach in many critical applications, especially for volatile and semi-volatile compounds [1-10]. Some of the known features associated with this prevalent analytical technique are improved chromatographic efficiency, relatively low cost, and high reliability.

Single dimensional GC with capillary column technology has been the right prescription for many critical separation needs. The high chromatographic efficiency delivered by single dimensional open tubular capillary GC has achieved much, yet more separation power is desired. The finite separation capability of this technique is an inherent constraint which has been a challenge to practitioners in dealing with complex matrices. Unlike packed column technology where hundreds of stationary phases are available to influence column selectivity, capillary column technology has limited stationary phase options such as siloxanes and functionalized siloxanes, polyethylene glycols, and variants of ionic liquids. Challenges continue to exist in several areas especially when dealing with complex matrices [11-12].

Some approaches that can be used to address the lack of selectivity due to the apparent lack of stationary phase choices are techniques like coupled column chromatography, selective tuning, column effluent splitting, or parallel chromatography. These techniques are made possible only by recent developments in advanced metal working processes. Metal injection moulding (MIM), is a highly efficient production process where powdered metal and binder are blended as a paste and

subsequently shaped by injection moulding. The technique can produce small complex parts with low tolerances. Diffusion-bonding technologies have resulted in a new generation of microfluidic devices that are compatible with capillary chromatography. One of the methods to fabricate microfluidic devices involve constructing a series of ultra-thin stainless-steel plates with the channels and the desired flow architectures precisely formed in the individual stainless-steel plates using laser milling techniques [13,14]. When the thin stainless-steel plates are fused together a multi-plate wafer is created. This multi-plate concept allows very complex flow systems to be fabricated with minimal void volume to preserve the quality of chromatography obtained. While metal is the ideal medium for an in-oven connecting device, it can be rather active or catalytic for reactive solutes such as amines, acids, and pesticides to name a few. Fortunately, many established techniques can deliver effective surface passivation, such as chemical and physical vapour deposition [15-17].

Planar microfluidics plays a crucial role in inter-column connectivity, in enabling successes for multi-dimensional GC (MDGC) to be practiced reliably, and in creating new possibilities to hyphenate multiple detectors to GC [18-22]. Planar microfluidic devices are used extensively throughout many applications described in this thesis. While metal microfluidics (MMF) devices have many advantages, channels in the chromatographic flow path for inter-column connectivity applications have some constraints. Current technology can create non-uniform flow paths that are limited in size of roughly 50  $\mu\text{m}$  in depth and 40  $\mu\text{m}$  wide. Issues related to void volume incurred from this process can have a negative impact on the quality of chromatography obtained. These factors preclude the use of narrow bore columns of 180  $\mu\text{m}$  or less. A potential strategy used to minimize peak broadening effects include using higher carrier gas flow rates in combination with open tubular columns with internal diameter  $\geq 250 \mu\text{m}$  to maintain chromatographic performance.

Unlike other approaches in analytical separation science, GC is compatible with a wide variety of detectors [23-25]. While universal detectors provide information on the totality of the sample, selective detectors have an important role to reduce analysis times, simplify quantification, and provide information on specific physiochemical properties. When correctly applied, selective detection can substantially ease the burden of separation imposed on the separation column, and is especially useful for increasingly complex and challenging sample matrices. Using this re-distributed analysis strategy, selective detection can be an enabler to high-speed GC and pave a way for the development of portable and hand-held analytical devices. Furthermore, by design, selective detection offers improved sensitivity for targeted compounds which is a highly sought-after attribute in contemporary analytical sciences. Improved sensitivity can reduce or eliminate the need for time-consuming sample pre-concentration. Therefore, research efforts conducted in this area are central to the capability and sustainability in GC development.

Amongst selective detection schemes, ultra-violet (UV) detection is a viable option with many attractive features. Its non-destructive nature is amendable for serial and multi-detection approaches. In addition, UV detection has high analyte selectivity and unlike mass spectrometry, operates without the requirement for reduced pressure environments which allows for quick system start-up. Another foundational driver is many organic compounds common in chromatographic separations show an absorption spectrum in the UV and visible region. Thus, GC-UV is indicative for both qualitative and quantitative analysis. Gas phase spectra can be generated which can be useful for provisional structural elucidation, especially when used in conjunction with MS. GC-UV has respectable analyte detectability with detection limits generally in the nanogram range.

Since the early 60s, efforts to employ UV detection with GC have been well reported in the literature by various technology pioneers and early adopters [26-43]. Recently, Schug et al. reported new endeavours to expand this field of practice by exploiting the vacuum UV (VUV) region in addition to the traditional UV range with a dedicated analytical detection system which provides simultaneous universal and selective gas phase detection in the picogram range. The detector optics are purged with dry high purity nitrogen of 99.999% or better and customized deconvolution software aids in peak identification. [44-46].

Despite many concerted efforts since its first description, the adoption rate of UV detection by practitioners has been slow to moderate. Plausible barriers that may have limited development include challenges associated with constructing suitable detector-GC interfaces, challenges encountered with light sources like additional time to reach stability, regressive decay of light intensity over time, alignment of light sources with the flow cell, design of the flow cell to achieve contemporary limits of detection, and options for light detection. In addition, accumulated void volume can have a negative impact on the quality of chromatography obtained. Finally, overall inertness of the sample flow path has limited several advances, especially for active compounds.

One of the key contributions made with this graduate research involves advancing knowledge in the area of GC-UV through interfacing of a contemporary diode array detector (DAD) initially designed for liquid chromatography (LC) repurposed for GC. This design required both an effective strategy for heat management and highly inert sample flow path [47-49]. The recently commercialized DAD detector based on a cartridge cell design with optofluidic waveguides renders improved light transmission with full spectral detection. The DAD can be highly advantageous for use with narrow chromatographic peaks encountered in GC especially with high data sampling rates up to 200 Hz. Increased sensitivity and selectivity can be achieved for many

classes of compounds with chromophores. The non-destructive nature of the DAD permits the incorporation of a second detector in series which provides information-rich chromatography without incurring extra analytical time or column effluent splitting which can reduce overall detectability.

Unlike use in LC, heat management is essential to successfully interface the DAD to a GC. To preserve the excellent chromatography obtained with high-resolution capillary columns, a novel heated cell was innovated and implemented. Apart from the self-aligning capability of the cell, one significant advantage involved the capability of heating the optical cell with positive temperature coefficient thermistors (PTC). PTC thermistors as heating devices are quickly gaining acceptance and are making a positive transformation in many sectors for numerous critical applications [50-53]. Compact PTC heaters provide consistent isothermal heat which is repeatable but not necessarily accurate particularly at temperatures exceeding 200 °C. The use of PTC heaters offers substantial benefits such as energy efficiency, safety in overheating, size, scalability, and discovery of new thermal management strategies. While analyte flow path inertness is not a central issue for LC due to the liquid mobile phase, in GC it is imperative to achieve the most inert flow path possible. Effective deactivation schemes were applied to ensure analytes are not absorbed or adsorbed in the optical cell employed by the DAD. By incorporating positive temperature coefficient technology into a commercial DAD detector and through successful passivation of the optical cell, the detector was made suitable for coupling with GC [54].

The logical choice of having a molecular spectroscopic detector like the DAD with contemporary planar microfluidic enabled GC is to employ the device in multi-dimensional GC and in hyphenated techniques. These pairing options improve separation, selectivity, and accuracy of analytical measurements. Without any doubt, hyphenating a separation technique like GC with

a spectrometric technique like MS has proven to be an essential development to sustain continual growth in chromatography [55-57]. Since the DAD is non-destructive, a novel hyphenated approach which incorporates a DAD in series with an MS and having the MS in tandem with an FID to GC was also successfully developed [58]. The combination of GC-DAD-MS/FID enhances selective detection by monitoring specific wavelengths by DAD and compound specific target ion fragments using Selected Ion Monitoring (SIM) Mode by MS. In parallel, the full spectrum obtained by the DAD and mass fragmentation patterns by the MS in SCAN mode are quite complementary, especially for structural elucidation [58]. For quantification, the simultaneous target wavelength/SCAN of the DAD and the SIM/SCAN of the MS simplifies the measuring process.

Another hyphenated technique explored in this study involved MDGC with the atomic emission spectrometric detector (AED). Although the AED is an atomic spectroscopic detector, its utility was investigated to further illustrate its complementary nature to molecular spectroscopy and the positive impact that planar microfluidic devices can deliver. Detectors which combine plasma excitation with optical emission spectroscopy have been used to detect a wide variety of analytes in chromatographic effluents with great success [59-64]. Unlike the ubiquitous flame ionization detector (FID) which measures simple gas-phase carbon-containing ions created in a hydrogen flame, the AED is broader in application. By design, the principle of detection is based on atomic emission. Despite requiring specialized skills to operate and the need for additional reagent gases, the strength of the AED lies in the detector's ability to simultaneously determine the atomic emission of elements as the analyte is eluted from the column. With a single analysis, significant information about a sample can be achieved. Limitations such as excessive carbon deposition in the plasma source can be overcome by MDGC through the option to selectively transfer, i.e. heart

cut only the analytes of interest to the AED and to backflush the matrix to vent to preserve chromatographic system fidelity. The synergy gained by combining MDGC with AED and planar microfluidics was demonstrated in the determination of elemental mercury in hydrocarbon matrices [65].

The development of detectors with microfluidic devices and hyphenating techniques described earlier was successfully applied to enhance the analytical capabilities of portable and transportable instruments. These analytical instruments play critical roles in providing relevant results, especially for in-field analysis. The study involved the coupling of three different gas phase detectors; a  $\mu$ DMS, a conventional DAD, and a micromachined thermal conductivity detector ( $\mu$ TCD) coupled to a micromachined GC. This effective design is able to provide rapid, sensitive, and selective detection for targeted volatile compounds in various matrices [66]. The tuneable selectivity rendered by the DAD and the  $\mu$ DMS, combined with temporal and spatial separation mechanisms substantially increased the analytical capabilities of the portable device [67-69]. This approach will catalyze further innovations in portable and eventually hand-held equipment.

In summary, one can predict with a high degree of certainty that combining advances in molecular absorption and elemental emission spectroscopy with hyphenated techniques enabled by microfluidic devices will play a vital role in proliferating GC. The research studies conducted on innovative assemblies of instrumentation, components, and methodologies have a positive impact in solving complicated separation and detection problems. Another expected outcome of this effort is that simple analytical solutions will emerge to the community of practice. Finally, further developments continue to have a positive transformational effect on the sustainability of the future of chromatography.



## 1.2 Scope of Thesis

This work has two major themes. The first theme involves exploring the articulated and unarticulated benefits associated with modern spectroscopic detection techniques in GC. A main effort of the research involves overcoming obstacles encountered in interfacing a contemporary DAD designed for LC in a manner that facilitates use as a selectable multi-wavelength spectroscopic detector for GC. Challenges in the areas of interconnectivity between the GC and the detector, on sample flow path inertness against active compounds, on critical heat management associated with analyte transfer between the GC and detector, and on the design and implementation of a heated optical cell that is suitable for both volatile and semi-volatile compounds with respectable sensitivity were overcome. Heat management and approaches in sample flow path deactivation are two critical areas of development as they are the Achilles heel of any gas phase analytical system. The improvement of chromatographic aspects related to the portability, selectivity, sensitivity, and throughput of analytical systems were sought after. The synergy gained from combining selective detection with contemporary planar microfluidic devices resulted in innovative analytical methods developed and implemented to address challenging problems encountered.

The second theme involves applying selective detection to ease the burden of separation traditionally imposed on the analytical column especially when the matrices of the samples are increasingly complex to tackle. Selective detection is an enabler to high-speed GC which is a critical component in the development of portable and hand-held analytical devices.

In the current research, the positive impact of using spectroscopic and spectrometric techniques with a particular focus on UV detection methods were studied. The effectiveness of combining of

a recently innovated tuneable UV based detector with other hyphenated techniques in conjunction with contemporary selective detectors such as the AED,  $\mu$ DMS, and the MS operating in the selected ion monitoring mode was reaffirmed and illustrated. Included in this work is the successful innovation, development, and implementation of various analytical methods that address demanding chromatographic needs that have been encountered by the community of practice.

## CHAPTER 2

### SINGLE WAVELENGTH UV DETECTION IN GAS CHROMATOGRAPHY

In **Chapter 2**, an innovative single wavelength GC-UV system was developed for the direct measurement of parts-per-trillion (v/v) levels of elemental mercury ( $\text{Hg}^0$ ) in air, natural gas, and light hydrocarbons.  $\text{Hg}^0$  can be released into the environment from a variety of natural sources, such as forest fires, volcanic eruptions, or anthropogenic activities including fossil fuel combustion and metal production. Analyzing  $\text{Hg}^0$  via GC has not been actively considered as an analytical technique. However,  $\text{Hg}^0$  possesses a favourable vapour pressure that makes it very suitable for this detection technique, especially when used with a UV detector equipped with a Hg lamp at 253.7 nm and an inert chromatographic sample flow path.

The single wavelength UV detector employed was a Reductive Compound Photometer (RCP) which was substantially modified to increase compatibility with capillary GC. RCP, also known as Reduction Gas Detector (RGD), was conceived as a GC detector for determination of trace carbon monoxide and hydrogen for the electronics industry. The compounds of interest are detected by proxy with photometric detection of  $\text{Hg}^0$ , which is liberated from the reaction of the analytes with mercuric oxide. Since the target analyte is  $\text{Hg}^0$ , the redundant mercuric oxide bed was eliminated. The inertness of the sample flow path was enhanced by heat tracing and deactivated fused silica tubing was incorporated. The rest of the critical components of the RCP were retained. With peak tailing caused by reactor kinetics or geometry eliminated, satisfactory performance was obtained.

While the RCP is an adequate detector for this novel application described, it has many limitations such as single wavelength light source of the mercury lamp, out-dated electronics designed in the 60s with vacuum tubes that caused substantial baseline drift over time, and has

inadequate thermal management for higher boiling compounds. The use of UV detection has many attractive features including its non-destructive nature which can be an enabler for serial and multi-detection approaches, analyte selectivity, and vacuum-free operation conditions. Compounds amenable to electronic spectroscopy contain electrons capable of being promoted from an occupied molecular orbital (usually a non-bonding  $n$  or bonding  $\pi$  orbital) to a greater potential energy unoccupied molecular orbital (anti-bonding orbitals like  $\pi^*$  or  $\sigma^*$ ). In UV, qualitative analysis can be executed with the acquisition of high-resolution spectra. Well defined gas phase spectra generated can be useful for compound identification and structural elucidation especially when used in conjunction with MS as described later in this study. Quantitative analysis can also be conducted with a respectable linear range of at least  $10^3$  by the Beer-Lambert law at a user-defined wavelength. GC-UV has respectable analyte detectability with detection limits generally in the nanogram range. Therefore, these factors are compelling drivers for the use of a contemporary DAD for use as a research detector platform to study the many benefits and impacts of UV as a GC detector as shown in the next chapter.

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### CHAPTER 3

## MULTI-WAVELENGTH MOLECULAR UV SPECTROSCOPY DETECTION IN GAS CHROMATOGRAPHY

The successful interfacing of a contemporary molecular spectroscopy-based DAD initially designed for LC to a GC is described in **Chapter 3**. DAD brings ultraviolet-visible spectroscopy (190 – 640 nm) onto the capillary GC timescale, enabling spectrophotometric detection of analytes with peak widths in the 3 to 5 s range. The recently commercialized DAD detector based on a cartridge cell design with optofluidic waveguides has improved light transmission with full spectral detection. Optimized light transmission and collection require the detector optics to have near flawless alignment yet protection from the sample flow path. The sample can deteriorate the optical window transmission through chemical etching or condensation. The self-aligned cartridge designed allows for efficient and effective replacement. The detector is also capable of interchanging flow cells with different path lengths of up to 60 mm with a dispersion volume ( $\sigma_v$ ) of up to 4  $\mu$ L. With full spectral detection at a sampling rate of up to 240 Hz and a 1024 diode array assembly, the DAD can be highly advantageous for use with narrow chromatographic peaks encountered in GC. Further, the detector enables simultaneous detection of up to 8 wavelengths over the UV/VIS range. Increased sensitivity and selectivity can be achieved for many classes of compounds including alkenes, dienes, sulfurs, and aromatics.

With modifications made to the detector, software, inter-column connectivity, and interfaces, the successful coupling of the DAD to a GC was demonstrated with an application of industrial significance; namely the measurement of carbon disulfide ( $\text{CS}_2$ ) in the workplace. Common detectors such as FID and TCD have relatively poor sensitivity for the detection of  $\text{CS}_2$ . As a result, specialized detectors such as FPD, SCD, or MS in SIM mode can provide a solution without the

need for pre-concentration techniques. There exists an unmet need for a direct measurement of ultra-trace levels of CS<sub>2</sub> using a low maintenance, sensitive, and selective detector. High throughput provides results for quick data-driven decisions necessary to protect workers and monitor both natural and industrial point sources. The technique can also be employed to indirectly measure the presence of residual fungicide like Mancozeb on fruits and vegetables for effective transportation and to monitor for human health concerns. GC-DAD provides a simplified, low cost, and highly reliable approach with a respectable detection limit of 93 pg of CS<sub>2</sub> on the column.

The non-destructive feature of the DAD allows an FID to be incorporated in series to provide information-rich chromatography. This arrangement delivers near-simultaneous selective and universal detection without increasing analytical time and without recourse to column flow splitting. The DAD is small in size and does not require make-up or optic purge gases. This fast and facile approach was effectively used for the direct measurement of 1,3-butadiene in complex matrices such as exhaust gas from internal combustion engines and workplace atmospheres. In industry, 1,3-butadiene is significant as it plays an active role as a reactant for rubber. Environmentally, this compound is of interest as it is a suspected human carcinogen.

With LC, the cell is maintained at ambient temperatures for obvious reasons. In contrast with GC, effective and accurate heat management of the transfer line and optical cell is critical to achieving repeatable retention times, prevent undesirable condensation which can cause peak distortion, and extend the volatility range of the analytes and associated matrices. Concurrently, the electronics and optics of the detector need to be shielded from the potential thermal crosstalk of the heated cell. Properly optimized, compounds with boiling point equivalent to hexadecene (285 °C) can be analyzed using the configuration described.

Novel concepts and strategies of heating the detector cell were further investigated to improve reliability and to simplify thermal process control. This typically involves the use of multiple components such as a heater, a feedback and control mechanism, and a safety device to prevent overheating. Amongst many options explored, the discovery and implementation of positive temperature coefficient (PTC) thermistor as a heater was found to be the most efficient.

Apart from the detector having a self-aligned light path, one of the significant advantages of this new heated cell design involves the capability of heating the cell up to 150 °C. This use of PTC heaters does not require additional requirements for control or regulating electronics. The technology adoption of PTC heaters as isothermal heating devices are increasing and making a positive transformation with their adaptation into numerous critical applications. The use of positive temperature coefficient heaters offers substantial benefits in critical aspects such as energy efficiency, safety in overheating, size, scalability, and the discovering of new thermal management strategies. By incorporating a PTC heater into a commercial diode array photometric detector, effective coupling to GC was achieved.

Another challenge when interfacing the DAD to a GC involved analyte inert flow path issues associated with the flow cell. With the original design, untreated fused silica and polyether ether ketone polymer tubing were used. While this is acceptable with LC, this design leads to sub-standard chromatographic performance in GC. As it is critical in ultra-trace analysis by GC to have a highly inert sample flow path the materials used need to be free of silanol groups and active sites. The presence of active sites and silanol groups can have a negative impact on chromatographic peak symmetry and system detection limit for the target analytes. Various techniques were used to deactivate the cell surface and interface that contact with the analytes. For example, the removal of surface silanol groups using 5% dichlorodimethylsilane in toluene followed by siliconization



with dichlorooctamethyltetrasiloxane to generate a hydrophobic and tightly bonded film was found to be effective [15-17].

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## CHAPTER 4

### SELECTIVE DETECTORS AND HYPHENATED TECHNIQUES

The use of a variable wavelength UV detector such as the DAD that is compatible with contemporary planar microfluidic enabled GC is a logical choice for combination with hyphenated or MDGC techniques. **Chapter 4** demonstrates the efficacy of this approach to improve separation, selectivity, sensitivity, and accuracy of the analytical measurements.

The most powerful separation technique in GC is capillary gas chromatography (CGC). CGC has made substantial contributions to increase the popularity of GC. This technique has many desired attributes such as high chromatographic efficiency, resolution, and performance reliability. Recent advancements in multidimensional gas chromatography (GC-GC) and comprehensive two-dimensional gas chromatography (GC×GC) enabled by planar microfluidic devices and deconvolution software aid in improvements in overall system selectivity. However, one key limitation is the limited choice of stationary phases or adsorbents available to achieve optimum peak capacity for the target analytes and matrices. The constraint imposed by stationary phases reduces the degree of separation orthogonality obtained between the two dimensions of separation. As a result, efforts in chromatographic and spectroscopic selectivity need to continue to be a key focus. One might argue convincingly that selectivity improvement is just as critical as enhancing sensitivity. If the analytes cannot be separated from sample interferences, improvements in sensitivity alone will not result in improved analyte detection, especially for increasingly complex sample matrices.

Amongst selective detection approaches for GC, the use of UV spectroscopy is a relevant option with many positive attributes as described in Chapter 3. In general, GC-UV has adequate analyte detectability with a detection limit in the nanogram range for compounds that are suitable for

detection. Another appealing factor of GC-UV is that the gas phase spectra obtained can be advantageously used to support structural elucidation, especially when applied in conjunction with other gold standard techniques like mass spectrometry (MS). The benefits of pairing GC with MS were recognized quite early by the pioneers in chromatography and spectrometry. As will be forever debated, the first attempt to interface a GC and a MS was accomplished either by *Holmes and Morrell* at Phillip Morris Inc. in Richmond, Virginia or by *R. Gohkle and F. McLafferty* at the Dow Chemical Company in Midland, Michigan in 1957 shortly after the development of gas-liquid chromatography by James and Martin in 1952. The combination of the two significant analytical techniques in a hyphenated configuration such as GC-quadrupole MS (qMS) allows a much more accurate chemical identification than either independent technique can offer. Limitations in MS include its inability to differentiate isomers or compounds with very similar fragmentation patterns, dealing with labile and low mass compounds, and identifying the minor constituents that are partly co-eluted with much larger peaks. In the cases cited, MS may fail to provide an absolute identification of compounds even with the availability of pure standards. As a result, further enhanced techniques for functional group identification, electronic transitions, or structures are required. A novel multi-hyphenated analytical strategy that exploits the combination of three different detectors was developed. This design is able to improve selectivity, sensitivity, confirmatory capability, and structural elucidation capabilities. This strategy was achieved by interfacing a user selectable multi-wavelength DAD equipped with a PTC heated optical cell to a GC. Taking advantage of the non-destructive nature of the DAD, the effluent from the DAD is split to the other two detectors; namely a qMS and an FID. The FID measures simple gas-phase carbon-containing ions created in a hydrogen flame.

The hyphenated and integrated configuration of GC-DAD-MS/FID is a highly potent approach for both the enhanced selective detection by DAD with specific wavelengths and the qMS operating in Selected Ion Monitoring (SIM) mode. With the DAD, “on-the-fly” (OTF) UV-Vis spectra can be generated with up to eight user-selectable wavelengths simultaneously monitored. Despite the OTF UV-Vis spectra obtained by the DAD over the range of 190 nm to 640 nm lack the fine structures required for complete compound identification, these spectra served as an aid for confirmatory and structural elucidation capabilities when coupled with electron impact mass fragmentations generated by the qMS. The FID provides uncomplicated and reliable quantitative responses for carbon-containing molecules as well as a thorough perspective on the matrices of the samples, particularly for fuels and lubricants. This strategy substantially improves analytical productivity and asset utilization.

Another hyphenated technique explored in this study involve MDGC with the AED. Although the AED is an atomic emission spectroscopic detector, its utility was investigated to further illustrate its complementary nature with molecular spectroscopy and illustrate the positive impact that planar microfluidic devices can offer. Detectors which combine plasma excitation with optical emission spectroscopy have been used to detect a wide variety of analytes in chromatographic effluents with great success including the measurement of organometallic mercuric compounds in environmental and biological matrices. By design, the principle of detection is based on the detection of atomic emissions. As molecules exit the chromatographic column, they enter a helium plasma where the high temperature is sufficient to break bonds and excite atoms to higher excited electronic states. The specific frequencies of light are emitted by the excited atoms as they transition to lower electronic states. The strength of the atomic emission detection lies in its ability to simultaneously determine the atomic emissions of various elements in the analyte. In addition,

atomic emission detection is able to deliver compound independent response. With a single analysis, much information about a sample can be achieved. With the AED, the formation of excess soot or fly-ash results from atomizing carbon compounds. This can be quite problematic and lead to detector fouling which degrades chromatographic performance. These limitations were successfully overcome by advantageously combining features inherent to MDGC such as the option to selectively transfer, i.e. heart cut only the target analytes to the AED, and the capability to backflush the matrix to vent if required to preserve chromatographic fidelity. The synergy of combining the many positive features of MDGC with AED was demonstrated with the measurement of  $\text{Hg}^0$  in hydrocarbon matrices. With microfluidic enhanced MDGC, a new height of analytical performance for the AED was attained.



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## CHAPTER 5

### MULTI-DETECTION CAPABILITIES IN MICROMACHINED GAS CHROMATOGRAPHY

**Chapter 5** is a strong testimonial to the knowledge gained in hyphenating DADs with planar microfluidic devices. Advances made in this sector were successfully applied to enhance the analytical capabilities of portable and transportable instruments. These analytical instruments play critical roles in providing relevant results, especially for in-field analysis. As an illustration, three detectors including a microfabricated electromechanical system based on radio frequency modulated ion mobility spectrometry, a conventional DAD, and a microfabricated TCD were successfully interfaced to a micromachined gas chromatograph. This design allowed for fast and targeted analysis of volatile organic compounds. With enhanced system selectivity derived from two tuneable selective detectors, the analytical platform offers powerful capabilities in detecting individual and various classes of volatile organic compounds with a typical analysis completed in the minutes. The use of a silicon micromachined injector affords fast injection to minimize band broadening. The micromachined TCD provides a universal response to virtually all analytes. In addition, the linear range for accurate analyte measurement was extended. The DAD allows the selective detection of compounds with chromophores while the differential mobility spectrometer uses the non-linear mobility dependence in strong radio frequency electric fields for ion filtering. This technique is able to selectively and sensitively target compounds that generate either positive or negative ions upon exposure to nickel<sup>63</sup> ionization. Positive and negative are measured simultaneously. With this hyphenated and selective detection strategy, confirmatory results can be realized if the target compounds are amenable to be detected by both detectors. Also, two orthogonal separating mechanisms in a single transportable analytical system were achieved. Advantaged synergy also includes leveraging the resolving power of GC to minimize charge

exchange in the ionization chamber of the differential mobility spectrometer for improved detector performance. The advent of a highly sensitive and tuneable selective detector such as the  $\mu$ DMS and the DAD when coupled with micromachined GC using conventional capillary columns was demonstrated to be a powerful technique.

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## FUTURE WORK

Additional research that can extend the work described in this thesis include:

- a) The use of solid-state lighting (SSL) either as a single or a multi-wavelength or an array multiplexed light source for molecular spectroscopy is a relevant topic for research. SSL is a type of lighting that uses semiconductor light-emitting diodes (LEDs), organic light-emitting diodes (OLED), or polymer light-emitting diodes (PLED) as sources of illumination rather than electrical filaments, plasma employed in arc lamps such as fluorescent lamps, or a gas. Unlike in incandescent bulbs, with SSL, light is emitted by solid-state electroluminescence [70]. The small mass of SSL devices provide higher resistance to shock and vibration compared to brittle glass tubes/bulbs and long thin filament wires. They also eliminate filament evaporation, time requires to attain stability for efficient response, and significantly increase the lifespan of the illumination device. These features make SSL ideal for portable or hand-held instruments and can substantially transform the current performance and reliability of benchtop lab equipment.
- b) The incorporation of the advanced light measuring devices to replace photodiode array techniques such as an electron multiplying charged couple device (EMCCD) or intensified charged couple device (ICCD) [71-73]. These devices can make a positive difference to maximize the signal-to-noise ratio. The low noise at high readout speeds could make these devices useful for techniques that require fast data sampling rate like GC×GC. Recently, the positive impact of these devices has been realized in several analytical techniques like Raman spectroscopy and fluorescence microscopy, especially under low light conditions.
- c) Despite recent advances in deactivation and passivation technologies, challenges remain for highly active compounds such as primary amines, furfurals, chlorinated phenols, and pesticides

to name a few. Innovations in deactivation techniques to further enhance inertness of components along the sample flow paths are relevant to explore and address the expected need for ultra-sensitive femtogram level analysis.

- d) While some successes were achieved in this area, miniaturization of the analytical instrument without compromising analytical capabilities must continue to meet future analytical needs for in-field and on-line analysis. Further advances in techniques such as metal injection moulding, light sources, and the detection schemes previously described can play critical roles as enablers for the development of a new generation portable and hand-held devices. Emerging approaches where all the critical analytical components integrated into one simplified platform are being experimented. The outside-in-focus in leveraging advances in other disruptive techniques such as 3D printing for the precise and rapid fabrications of components can accelerate hardware development. Miniaturization is a vital element in ensuring the success and sustainability of the technique for decades ahead.
- e) The development of “smart” detectors capable of conducting self-diagnostics and self-correcting within a pre-defined range of critical parameters. This development would ease the burden on analysts and operators, improves reliability, and reduce the cost-of-ownership.
- f) The development of relevant applications to reinvigorate chromatography and to tackle increasingly complex sample matrices. Three-dimensional separations such as GC-GC- $\mu$ DMS, GC $\times$ GC- $\mu$ DMS, GC- $\mu$ DMS- $\mu$ DMS, or GC- $\mu$ DMS- $\mu$ MS are worth investigating to offer both improved selectivity and sensitivity for target compounds in complex sample matrices and for throughput enhancements.

## REFERENCES

- [1] K. Robards, P.R. Haddad, P. Jackson, *Principles and Practice of Modern Chromatographic Methods*, Elsevier Science, London, 2004.
- [2] G.T. Seaborg, G. Higgins, in L.S. Ettre and A. Zlatkis Editors, *75 Years of Chromatography – A Historical Dialogue*, Elsevier Science, Amsterdam, 1979.
- [3] L.S. Ettre, Development of chromatography, *Anal. Chem.* 43 (1971) 20A-28A.
- [4] L.S. Ettre, C. Horvath, Foundations of modern liquid chromatography, *Anal. Chem.* 47 (1975) 422A-446A.
- [5] L.S. Ettre, 1941-1951: The golden decade of chromatography, *Analyst* 116 (1991) 1231-1245.
- [6] H. Gordon, The discovery of partition chromatography. A personal view, *Analyst* 116 (1991) 1245-1251.
- [7] L. Zechmeister, L. Chohnoky, *Principles and Practice of Chromatography*, Chapman and Hall, London, 1941.
- [8] C.W. Gehrke, R.L. Wixom, E. Bayer, *Chromatography – A Century of Discovery 1900-2000*, Elsevier Science B.V., Amsterdam, 2001.
- [9] C. Poole, *The Essence of Chromatography*, Elsevier Science B.V., Amsterdam, 2003.
- [10] R. Grob, *Modern Practice of Gas Chromatography*, John Wiley & Sons, Inc., New York, 1995.
- [11] W. Jennings, *Applications of Gas Capillary Chromatography*, Marcel Dekker, New York, 1981.
- [12] W. Jennings, E. Mittlefehldt, P. Strempel, *Analytical Gas Chromatography*, Academic Press, New York, 2006.
- [13] P. Dawes, B. Barnett, R. Hibbert, *Proceedings of the 34<sup>th</sup> International Symposium on Capillary Chromatography, Poster, Riva Del Garda, 2010*, Sandra, P., Ed.; Pat Sandra Publisher, Kortrijk, 2010.
- [14] R. Freeman, P. Dawes, B. Barnett, R. Hibbert, *Proceedings of the 35<sup>th</sup> International Symposium on Capillary Chromatography, Poster, San Diego, 2011*, CASSS publisher, San Diego, 2011.
- [15] D. Smith, *Thin Film Deposition – Principles and Practice*, McGraw-Hill, New York, 1995.



- [16] D. Dobkin, M. Zuraw, *Principles of Chemical Vapour Deposition*, Kluwer Academic Publishers, Dordrecht, 2003.
- [17] J. Maham, *Physical Vapor Deposition of Thin Films*, John Wiley & Sons, New York, 2000.
- [18] B. Quimby, J. McCurry, W. Norman, Milestones in Chromatography, *LC-GC North America* 25 (2007) 137-141.
- [19] J. Luong, R. Gras, R.A. Shellie, H.J. Cortes, Applications of planar microfluidic devices and gas chromatography for complex problem solving, *J. Sep. Sci.* 36 (2013) 182-191.
- [20] J. Luong, R. Gras, M. Hawryluk, R.A. Shellie, H.J. Cortes, Multidimensional gas chromatography using microfluidic switching and low thermal mass gas chromatography for the characterization of targeted volatile organic compounds, *J. Chromatogr. A* 1288 (2013) 105-110.
- [21] J. Luong, R. Gras, H.J. Cortes, R. Mustacich, Low thermal mass gas chromatography: Principle and Applications, *J. Chromatogr. Sci.* 44 (2006) 219-226.
- [22] J. Luong, R. Gras, R.A. Shellie, H.J. Cortes, Direct measurement of part-per-billion levels of dimethyl sulfoxide in water by gas chromatography with stacked injection and chemiluminescence detection, *J. Sep. Sci.* 35 (2012) 1486-1493.
- [23] R. Scott, *Chromatographic Detectors – Design, Function, and Operation*, Marcel Dekker Inc, New York, 1996.
- [24] M. Dressler, *Selective Gas Chromatographic Detectors*, Elsevier, Amsterdam, 1986.
- [25] H. Hill, D. McMinn, *Detectors for Capillary Chromatography*, John Wiley & Sons, Inc., New York, 1992.
- [26] W. Kaye, Far-ultraviolet spectroscopic detection of gas chromatograph effluent, *Anal. Chem.* 34 (1962) 287–293.
- [27] D.J. Bornhop, L. Hlousek, M. Hackett, H. Wang, G.C. Miller, Remote scanning ultraviolet detection for capillary gas chromatography, *Rev. Sci. Instrum.* 63 (1992) 191–201.
- [28] D.J. Bornhop, G. Verga, Gasoline analysis by rapid scanning absorbance detection and capillary gas chromatography, *Trend Anal. Chem.* 11 (1992) 194–198.
- [29] D.J. Bornhop, J.G. Wangsgaard, GC-UV: capillary gas chromatography with rapid scanning ultraviolet detection, *J. High Resolut. Chrom.* 14 (1991) 344–347.

- [30] M. Hackett, H. Wang, G.C. Miller, D.J. Bornhop, Rapid scanning UV–vis detection for capillary gas chromatography using a remote flow cell, *J. Chromatogr. A* 695 (1995) 243–257.
- [31] V. Lagesson, L. Lagesson-Andrasko, Arrangement at a gas flow through cell for spectrophotometric analysis of chemical compounds, **U. S. Patent 4,668,091A**, May 26, 1987.
- [32] V. Lagesson, J.M. Newman, Microcolumn gas chromatography with ultraviolet detection and identification using a photodiode array spectrophotometer, *Anal. Chem.* 61 (1989) 1249–1252.
- [33] L. Lagesson-Andrasko, V. Lagesson, J. Andrasko, The use of gas-phase UV spectra in the 168–330 nm wavelength region for analytical purposes. 1. Qualitative measurements, *Anal. Chem.* 70 (1998) 819–826.
- [34] H.V. Lagesson, A. Nilsson, C. Tagesson, Quantitative determination of compounds adsorbed on indoor dust particles using GC-UV and GC-MS after thermal desorption, *Chromatographia* 52 (2000) 621–630.
- [35] H.V. Lagesson, L. Lagesson-Andrasko, J. Andrasko, F.J. Baco, Identification of compounds and specific functional groups in the wavelength region 168–330 nm using gas chromatography with UV detection, *J. Chromatogr. A* 867 (2000) 187–206.
- [36] V. Lagesson, L. Lagesson-Andrasko, Device in a gas flow cell and a method of analyzing chemical substances by means of the gas flow cell, **U. S. Patent 6,305,213 B1**, Oct. 23, 2001.
- [37] A. Nilsson, V. Lagesson, C.G. Bornehag, J. Sundell, C. Tegesson, Quantitative determination of volatile organic compounds in indoor dust using gas chromatography-UV spectrometry, *Environ. Int.* 31 (2005) 1141–1148.
- [38] D.G. Hatzinikolaou, V. Lagesson, A.J. Stavridou, A.E. Pouli, L. Lagesson-Andrasko, J.C. Stavrides, Analysis of the gas phase of cigarette smoke by gas chromatography coupled with UV-diode array detection, *Anal. Chem.* 78 (2006) 4509–4516.
- [39] T. Cedron-Fernandez, C. Saenz-Barrio, S. Cabredo-Pinillos, I. Sanz-Vicente, Separation and determination of volatile compounds in synthetic wine samples by gas chromatography using UV–visible molecular absorption spectrometry as detector, *Talanta* 57 (2002) 555–563.
- [40] A. Nilsson, Novel technique for analyzing volatile compounds in indoor dust, Linköping University, Sweden, 2004 (Thesis).
- [41] J. Merritt, F. Comendant, S.T. Abrams, V.N. Smith, Process gas chromatograph with ultraviolet detector, *Anal. Chem.* 35 (1963) 1461–1464.
- [42] M. Novotny, F.J. Schwende, M.J. Hartigan, J.E. Purcell, Capillary gas chromatography with ultraviolet spectrometric detection, *Anal. Chem.* 52 (1980) 736–740.

- [43] M. Kube, M. Tierney, D.M. Lubman, Ultraviolet–visible diode-array spectrophotometer as a detector for gas chromatography, *Anal. Chim. Acta* 171 (1985) 375–379.
- [44] K.A. Schug, I. Sawicki, D.D. Carlton, H. Fan, H.M. McNair, J.P. Nimmo, P. Kroll, J. Smuts, P. Walsh, D. Harrison, Vacuum ultraviolet detector for gas chromatography, *Anal. Chem.* 86 (2014) 8329–8335.
- [45] L. Bai, J. Smuts, P. Walsh, H. Fan, Z. Hildenbrand, D. Wetz, K.A. Schug, Permanent gas analysis using gas chromatography with vacuum ultraviolet detection, *J. Chromatogr. A* 1388 (2015) 244–250.
- [46] H. Fan, J. Smuts, L. Bai, P. Walsh, D.W. Armstrong, K.A. Schug, Gas chromatography-vacuum ultraviolet spectroscopy for analysis of fatty acid methyl esters, *Food Chem.* 194 (2016) 265–271.
- [47] R. Gras, J. Luong, R.A. Shellie, Direct Measurement of trace elemental mercury in hydrocarbon matrices by gas chromatography with ultraviolet photometric detection, *Anal. Chem.* 87 (2015) 11429–11432.
- [48] R. Gras, J. Luong, R.A. Shellie, Gas chromatography with diode array detection in series with flame ionisation detection, *J. Chromatogr. A* 1500 (2017) 153–159.
- [49] R. Gras, J. Luong, R.A. Shellie, Gas chromatography and diode array detection for the direct measurement of carbon disulfide in challenging matrices, *Anal. Methods*, 9 (2017) 3908–3913.
- [50] W. Heywang, Semiconducting barium titanate, *J. Mater. Sci.* 6 (1971) 1214–1224.
- [51] R. Musat, E. Helerea, Characteristics of the PTC heater used in automotive HVAC systems, *IFIP Adv. Inf. Commun. Technol.* 314 (2010) 461–468
- [52] Y.H. Shin, S.K. Ahn, S.C. Kim, Performance characteristics of PTC elements for an electric vehicle heating system, *Energies* 9 (2016) 813–821.
- [53] O. Man, J. Duck, T. Sung, Positive temperature coefficient heater, **US Patent 8115146 B2**, February 12, 2012.
- [54] R. Gras, J. Luong, M. Pursch, R. Shellie, Positive temperature coefficient compensating heating for analytical devices, *Anal. Chem.* 90 (2018) 6426–6430.
- [55] D. Sparkman, Z. Penton, F. Kitson, *Gas Chromatography and Mass Spectrometry: A Practical Guide*, Second Edition, Academic Press, Oxford, 2011.
- [56] R. Hites, Development of gas chromatographic mass spectrometry, *Anal. Chem.* 14 (88) 6955–6961.

- [57] R. Gohlke, F. McLafferty, Early gas chromatography/mass spectrometry, *J. Am. Soc. Mass Spectrom.* 4 (1993) 367-371.
- [58] R. Gras, J. Luong, P. Haddad, R.A. Shellie, Gas chromatography with simultaneous detection: Ultraviolet spectroscopy, flame ionization, and mass spectrometry, *J. Chromatogr. A* 1563 (2018) 171-179.
- [59] P. Wylie, B. Quimby, Applications of gas chromatography with an atomic emission detector, *J. High Resolut. Chromatogr.* 12 (1989) 813-818.
- [60] A.J. McCormack, S. Tong, W. Cooke, Sensitive selective gas chromatography detector based on emission spectrometry of organic compounds, *Anal. Chem.* 37 (1965) 1470-1476.
- [61] L. Ebdon, S. Hill, R. Ward, Directly coupled chromatography – A review - Atomic spectroscopy – Part I, *Analyst*, 111 (1986) 1113-1138.
- [62] B. Quimby, M. Delaney, P. Uden, R. Barnes, Determination of aqueous chlorination products of humic substances by gas chromatography with microwave plasma emission detection, *Anal. Chem.*, 52 (1980) 259-263.
- [63] R. Brown, S. Northway, R. Fry, Inductively coupled plasma as a selective gas chromatographic detector for nitrogen containing compounds, *Anal. Chem.* 53 (1981) 934-936.
- [64] P. Uden, *Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy*, American Chemical Society Symposium Series 479, 1992.
- [65] R. Gras, J. Luong, R.A. Shellie, Direct measurement of elemental mercury using multi-dimensional gas chromatography with microwave induced helium plasma atomic emission spectroscopy, *ACS Earth and Space Chem.* 2 (2018) 471-478.
- [66] R. Gras, J. Luong, R.A. Shellie, Miniaturized micromachined gas chromatography with universal and selective detectors for targeted volatile compounds analysis, *J. Chromatogr. A* article in press, September 2018, doi.org/10.1016/j.chroma.2018.08.064.
- [67] A. Shvartsburg, *Differential Mobility Spectrometry*, CRC Press, Boca Raton 2009.
- [68] G. Eiceman, Z. Karpas, *Ion Mobility Spectrometry*, CRC Press, Boca Raton, 1<sup>st</sup> ed., 1994.
- [69] G. Eiceman, Z. Karpas, *Ion Mobility Spectrometry*, CRC Press, Boca Raton, 2nd ed., 2005.
- [70] A. de Almeida, B. Santos, B. dePaolo, M. Quicheron, Solid state lighting review – Potential and challenges in Europe, *Renew Sust. Energ. Rev.* 34 (2014) 30-48.
- [71] M. Crawford, LEDs for solid-state lighting: Performance challenges and recent advances, *IEEE J. Sel. Top. Quantum Electron.* 15 (2009) 1028-1040.

[72] R. Haitz, J. Tsao, Solid-state lighting – Why it will succeed, and why it won't be overtaken, *Optik & Photonik*, 6 (2011) 26-30.

[73] A.J. Theuwissen, *Solid-State Imaging with Charge-Coupled Device*, Kluwer Academic Publisher, Dordrecht, 2006.

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